

Oxidation and sulfonation of cellulosics

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Received: 8 June 2007 / Accepted: 15 November 2007 / Published online: 5 December 2007
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Abstract Bleached hardwood (HW) kraft pulp and derived nanocellulosic structures were modified by a periodate oxidation followed by treatment with sodium bisulfite to yield the corresponding C2/3 sulfonates. The impact of this oxidative–reductive protocol on the chemical and physical properties of cellulose was evaluated by determining physical dimensions, functional groups, and their water absorbency properties. It was found that the water absorbency of cellulosic material can be enhanced by 8.0–199.0% with this oxidation/sulfonation protocol. Distinct differences were observed between sulfonated pulp fibers and nanocellulosic structures, with the latter exhibiting relatively higher water retention values (WRV).

Keywords Cellulose · Nanostructures ·
Periodate oxidation · Sulfonation ·
Water retention

Introduction

Cellulose is the most abundant renewable biopolymer in nature and it has the potential to become a key resource in the development of sustainable biofuels and biomaterials (Ragauskas et al. 2006). Although traditionally employed for paper production and some key commodity polymers, the chemistry of cellulose and its applications are undergoing a renaissance (Klemm et al. 2005). Recent studies have demonstrated its applicability as a value added material for improving the physical properties of composites while addressing many life cycle analysis issues (Huda et al. 2006; Eichhorn et al. 2001; Toriz et al. 2005). As an extension of these effects, cellulosic whiskers have been incorporated into several polymeric matrixes and shown to enhance strength and surface properties (Pu et al. 2007; Kvien et al. 2005; Samir et al. 2005).

The functionalization of cellulosic fibers further broadens the potential application of this biopolymer (Abdelmouleh et al. 2002; Roman and Winter 2006). For example, the grafting of acrylic groups onto cellulose has been shown to enhance the water absorbing properties of cellulosic fibers (Margutti et al. 2002; Gurdag et al. 2001). An alternative method for enhancing fiber charge is to employ 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) to oxidatively generate additional carboxylic acid groups (Saito et al. 2005, 2006). Saito and Isogai (2005) increased fiber charge by 150% for a hardwood bleached kraft pulp

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using TEMPO-mediated oxidation with NaClO and observed enhancing dry and wet tensile indices of paper test sheets by 30–200%. TEMPO oxidation of HCl-generated cellulose whiskers has also been recently reported, and in water these oxidized whiskers exhibited liquid crystal behavior and did not flocculate (Habibi et al. 2006).

An alternative approach for enhancing cellulosic fiber charge is to utilize sodium periodate to oxidatively cleave the C-2,3 hydroxyl groups of the glucose repeating unit of cellulose yielding the corresponding dialdehyde (Calvini et al. 2006; Kim and Kuga 2002; Kim et al. 2000; Kim and Shigenori 1999). Depending upon the extent of reaction, C-2,3 hydroxyl periodate oxidative cleavage of cellulose leads to a water-insoluble 2,3-dialdehyde cellulose derivative. Chlorite oxidation of 2,3-dialdehyde cellulose to the corresponding dicarboxylic acid has been used to prepare novel cellulose chromatography packing material (Kim et al. 2004). Alternatively, Shet and Wallajapet have reported that dialdehyde cellulose reacted with sodium bisulfite yields sulfonated cellulose. Sulfonated cellulose fibers were reported to significantly increase dry and wet tensile strength as well as water retention values (Shet and Wallajapet 1997). Herein we report the oxidation and sulfonation of cellulosic fibers and nanodimensional cellulose and their water absorbent properties. Our data demonstrated that selectively sulfonated cellulose exhibit enhanced absorbent properties.

Experimental

Materials

A never dried ECF fully bleached hardwood (HW) kraft pulp (Sample: C0) was employed in this study. All other chemicals were purchased from EM Science (NJ, USA), Aldrich or Fluka Chemical Company and used as received.

Preparation of cellulose nanospheres

Cellulose nanospheres were prepared from kraft fibers (30.00 g, ECF HW kraft pulp) following a literature procedure (Zhang et al. 2007). In brief, the pulp was milled through a Wiley mill equipped with a

20 mesh screen. The milled pulp was then transferred into a 5.00 M NaOH solution (250.00 mL) and heated to 80 °C for 3 h. The slurry was then filtered and thoroughly washed with deionized (DI) water until the wash water was pH neutral. The resulting cellulosic fibers were air-dried, added to DMSO (250.00 mL) and stirred at 80 °C for 3 h. Subsequently, the fibers were filtered and washed with DI water (3×250.00 mL). The washed fibers were then transferred into an HCl–H₂SO₄ aqueous solution (100.00 mL 12.1 N HCl, 300.00 mL 36.0 N of H₂SO₄, 600.00 mL of H₂O) and the solution was sonicated with a VWR 150 HT ultrasonicator at 80 °C for 8 h with mechanical mixing.

After the hydrolysis process, the fiber slurry became a milky colloid suspension. The mixture was centrifuged and the isolated solid fraction was dispersed in 250.00 mL DI water, mixed and then centrifuged at 2000 Relative Centrifugal Force (RCF), followed by decanting of the top clear layer. After the initial washing, the nancellulosic particles were neutralized with 2.00 N NaOH to pH 7.0 and further washed with DI water (3×150.00 mL) via dispersion–centrifuging–decanting of clear top layer. Afterward, the cellulosic particles were dialyzed (Spectra/Por dialysis membrane MWCO:1000) against water and subsequently freeze dried to give cellulose nanospheres I (Sample: C1; 67% yield, average diameter = 360 nm). Cellulose nanospheres I was used for the second hydrolysis or stored at 5 °C for further testing. Ultrasonication of the cellulose nanospheres I in a dilute H₂SO₄–HCl solution (pH 2.5, 2.5% cellulose by weight solution) yielded, after a comparable workup procedure cellulose nanospheres II (Sample: C2; 60% yield, average diameter = 80 nm).

Preparation of cellulose whiskers

An aqueous suspension of cellulose whiskers was prepared following the procedure outlined by Nelson and Deng (2006). In brief, the HW ECF-bleached kraft pulp was Wiley milled through a 20 mesh screen. The milled pulp (40.00 g oven-dried wt) was then treated with 64% sulfuric acid solution (700.00 mL) at 45 °C for 45 min. The reaction suspension was then diluted 10-fold with DI water to terminate the hydrolysis reaction. The suspension was concentrated by allowing the solids to settle overnight and then collecting the solids from solution with a minimal amount of water.

Excess acid was removed by washing with DI water (5×100.00 mL) and centrifugation at 25,900 RCF for 30 min. The sample was then dialyzed (Spectra/Por membrane, MWCO 50 K) against DI water for several days until the eluent was neutral. To separate flocculated whiskers, the suspension was continuously sonicated (Heat Systems-Ultrasonics W-385 sonicator) for 35 min at 0 °C. The suspension was treated with a bed resin (Sigma TMD-8, 1 g for every 10 mL of suspension) for 48 h and then filtered through ashless Whatman 541 filter paper. The micrographs indicated that the whiskers (Sample: C3) had an average length of 300 nm, and width of 8 nm. The yield of the whiskers was 33%.

Sodium periodate oxidation of cellulotics

A cellulosic sample (2.50 g oven-dried, wt) was mixed with 100.00 mL of aqueous pH 4.0 sodium periodate (Low Oxidation: 0.30 g, 1.40 mmol; High Oxidation: 0.60 g, 2.80 mmol) solution warmed to 38 °C. The mixture was then stirred for 1 h under a nitrogen atmosphere in the absence of light. After completion of the oxidation, the cellulose fibers were recovered by filtration or centrifugation, dispersed in DI water (15.00 mL), agitated for about 15 min and filtered. This work-up procedure was repeated four additional times and provided the 2,3-dialdehyde products of ECF HW cellulose, nanospheres and whiskers in 95–99% yield (Samples: C0LO, C0HO, C1LO, C1HO, C2LO, C2HO, C3LO, C3HO; Note: ECF HW cellulose, nanospheres I, nanospheres II, and whiskers = C0, C1, C2, and C3; low oxidized cellulotics = LO; high oxidized cellulotics = HO).

Sulfonation of 2,3-dialdehyde cellulose

The low oxidized cellulose (2.50 g, oven-dried wt) was dispersed in DI water (100.00 mL) at 22 °C and was treated with sodium bisulfite (0.50 g, 4.80 mmol). After stirring the mixture for 2 h, the slurry was centrifuged, decanted and diluted with DI water (5×100 mL). The wash–centrifuge–decant process was repeated 5 times and gave the corresponding low oxidation/sulfonated cellulose product (Samples: CXLOS, $X = 0, 1, 2, 3$; S indicates that cellulosic has been sulfonated) with a yield from 91 to 96%.

The high oxidized cellulose (2.50 g, oven-dried wt) was dispersed in DI water (100.00 mL) at 22 °C and was treated with sodium bisulfite (1.0 g, 9.60 mmol). After stirring the mixture for 2 h, the slurry was worked-up in the same manner as described above yielding the high oxidation/sulfonation product (Samples: CXHOS, $X = 0, 1, 2, 3$; S indicates that cellulosic has been sulfonated) in 86–92% yield.

Characterization of cellulotics

An aqueous nanocrystalline cellulose suspension (0.03%) was prepared by mixing nanoparticles into DI water which was then analyzed with a Malvern 3000 Zetasizer. Scanning electron microscopy (SEM) was performed using a LEO 1530 thermally assisted field emission (TFE) microscope; the samples were freeze dried and coated with gold. High-resolution transmission electron microscopy (TEM) was carried out with a JEOL 100 CX II microscope at 100 kV; cellulose whiskers were dried on a carbon coated Lacey TEM grid and stained with 25% uranyl acetate solution for 30 min. Fiber length was measured by fiber quality analyzer (FQA, OpTest Equipment Inc.), with an average experimental error of 0.01.

Atomic force microscopy (AFM) was performed using a Digital Instruments Nanoscope Dimension 3100 scanning probe microscope and a Nanoscope III controller. Images ($1 \mu \times 1 \mu$) were collected using a tapping mode etched silicon tip, with a nominal spring constant of 5 N/m and a nominal frequency of 150 kHz. ^{13}C -CP/MAS NMR spectra were recorded at room temperature on a Bruker Advance/DMX-400 operating at 100.06 MHz using a MAS WB CP BB VTN-BL 4 mm probe and ZrO_2 rotors (Pu et al. 2006). The MAS spin rate was 5 kHz. Acquisition was performed with a CP pulse sequence using a 4.5 μs pulse, 2.0 ms contact pulse, a 3.0 s delay between repetitions and 5,000 scans/sample.

Carboxyl and sulfonate group content and copper number

The acid group content of the cellulotics was determined by a published conductometric titration method (Lloyd and Horne 1993). Copper number was determined following Tappi standard method T 430

(Tappi Standard T430). Both the group content and copper number were analyzed in duplicate for each sample giving results with errors of less than ± 3 and $\pm 5\%$, respectively.

Water retention value (WRV) of celluloses

Pulp water retention values were determined by using Tappi Useful Method 256 Water Retention Value (Tappi Useful Methods 1991). This methodology involves a pulp mat formed by draining dilute pulp slurry on a fine mesh screen in a centrifuge cup. The pulp mat is prepared at a fixed basis o.d. weight of 0.250 ± 0.050 g. The pulp pad is then centrifuged at 900 g for 30 min. The wet pad was weighed after centrifuging, dried at 105°C , and then reweighed. The WRV is calculated as the amount of water by weight retained in the pad after centrifuging per oven dried (o.d.) weight of fibers (Eq. 1).

$$\text{WRV} = \frac{W_w - W_d}{W_d} \times 100\% \quad (1)$$

W_w is the weight of the wet sample after centrifuging, and W_d is that of dry sample. The tests were done in quadruplicate, and standard deviation of 95% confidential level was used for the experimental error evaluation.

Results and discussion

The modification of cellulotics by periodate oxidation followed by sulfonation was examined using a

hardwood ECF bleached kraft fiber, cellulosic whisksers and cellulose nanospheres (Scheme 1).

The effects of periodate oxidation and subsequent sulfonation on cellulosic fibers and cellulosic nanoparticles were initially assessed by determining the carbonyl and acid group content of these samples. Röhrling et al. (2002) has reported a linear relationship between the carbonyl group content and copper number ($\text{Cu}^\#$), as shown in Eq. 2.

$$\begin{aligned} \text{Carbonyl Group Content (mmol/100 g o.d. pulp)} \\ = (\text{Cu}^\# - 0.07)/0.6 \end{aligned} \quad (2)$$

In this study, the copper number of the oxidized cellulotics was experimentally measured and then converted to carbonyl group content (Table 1). The treated cellulose nanospheres (I and II) and whisksers had much higher initial copper numbers compared to the original ECF HW kraft pulp due to cleavage of cellulose chains and formation of the corresponding aldehyde end-groups originating from the acid hydrolysis procedure. As a result of periodate oxidation, both cellulose fibers and nanoparticles exhibited increases in copper number ranging from ~ 80 to 650% for the low charge of periodate and from 159 to 948% for the high oxidative conditions.

The C2,3-dialdehyde cellulotics were then treated with sodium bisulfite to yield the corresponding sulfonated cellulotics. The total acid group content of these materials was determined by conductometric titrations and these results are summarized in Table 2. These results indicate that the total acid

Scheme 1 Oxidation and sulfonation of cellulotics (2.50 g)

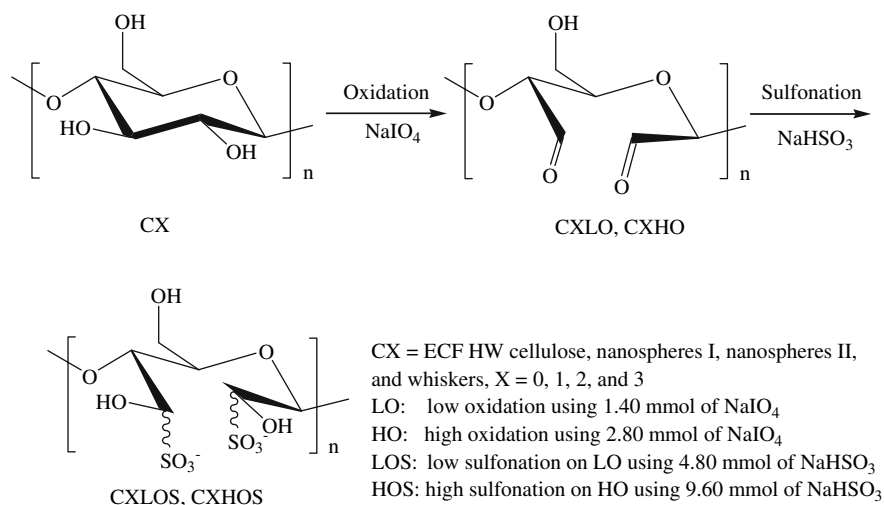


Table 1 Copper number and corresponding carbonyl conversion of various samples

Samples	Copper number	Carbonyl group (mmol/100 g o.d. pulp)
ECF HW cellulose (C0)	0.68	1.02
ECF HW cellulose LO (C0LO)	5.11	8.40
ECF HW cellulose HO (C0HO)	7.13	11.77
Cellulose nanospheres I (C1)	5.07	8.33
Cellulose nanospheres I LO (C1LO)	9.18	15.18
Cellulose nanospheres I HO (C1HO)	13.14	21.78
Cellulose nanospheres II (C2)	5.38	8.85
Cellulose nanospheres II LO (C2LO)	9.96	16.48
Cellulose nanospheres II HO (C2HO)	14.86	24.65
Cellulose whiskers (C3)	3.56	5.82
Cellulose whiskers LO (C3LO)	7.62	12.58
Cellulose whiskers HO (C3HO)	10.45	17.30

Note: LO = low oxidized cellulotics; HO = high oxidized cellulotics

group content decreased by 6.5–24.2% after the periodate oxidation and increased by 77.5–203.4% after sulfonation. Obviously, sulfonation of the cellulotics treated with a high periodate charge resulted in a higher total acid group content than the low periodate charge.

The starting, oxidized and sulfonated cellulotics were characterized by ^{13}C CP-MAS NMR. The oxidized cellulose data was consistent with Varma et al. (1997) ^{13}C CP-MAS NMR spectra data for periodate oxidized cellulose. In cellulose, the signals from δ 72.5 to 78.5 ppm are assigned to C2, C3, and C5 of cellulose (Pu et al. 2006) and the change in signal intensity was determined and summarized in Table 3. There were integration differences between the oxidized and original cellulosic samples, while there were only slight differences between the oxidized and sulfonated cellulosic samples in the same region. These results are consistent with bond rupture and sulfonation of the C-2 and C-3 positions of select glucose rings.

The physical size effects of the oxidized and sulfonated cellulotics are summarized in Tables 4 and 5.

Table 2 Total acid groups measurements and water retention values (WRV) of various cellulosic samples

Samples	Total acid groups	WRV ^a
ECF HW cellulose (C0)	2.00	0.415
ECF HW cellulose LO (C0LO)	1.87	0.345
ECF HW cellulose LOS (C0LOS)	3.55	0.448
ECF HW cellulose HO (C0HO)	1.79	0.378
ECF HW cellulose HOS (C0HOS)	5.90	0.647
Cellulose nanosphere I (C1)	2.06	0.402
Cellulose nanosphere I LO (C1LO)	1.89	0.394
Cellulose nanosphere I LOS (C1LOS)	4.05	1.201
Cellulose nanosphere I HO (C1HO)	1.76	0.408
Cellulose nanosphere I HOS (C1HOS)	6.15	0.956
Cellulose nanosphere II (C2)	2.11	0.398
Cellulose nanosphere II LO (C2LO)	1.94	0.376
Cellulose nanosphere II LOS (C2LOS)	4.42	0.984
Cellulose nanosphere II HO (C2HO)	1.87	0.363
Cellulose nanosphere II HOS (C2HOS)	6.36	0.837
Cellulose whisker (C3)	2.07	0.422
Cellulose whisker LO (C3LO)	1.60	0.348
Cellulose whisker LOS (C3LOS)	3.92	1.112
Cellulose whisker HO (C3HO)	1.57	0.336
Cellulose whisker HOS (C3HOS)	6.28	0.823

Note: LO = low oxidized; HO = high oxidized; LOS = low sulfonation of low oxidized cellulotics; HOS = high sulfonation of high oxidized cellulotics

^a mmol/100 g o.d. fibers

These results indicate that the sulfonated samples were shorter than the oxidized samples and the oxidized samples were in turn shorter than the unoxidized samples.

TEM analysis indicates that the shape of the oxidized celluloses nanospheres was deformed, gradually losing their original spherical shapes with increased oxidation/sulfonation. These changes in shape for the cellulose nanospheres were extended after sulfonation, and the formation of rod-like aggregates as shown in Fig. 1.

Amplitude images from atomic force microscopy (Fig. 2.) indicate that the initial ECF hardwood Kraft pulp was fibrillar, while the periodate oxidized and the oxidized/sulfonated ECF pulp fibers had less well-defined structures with little evidence

Table 3 Change of ^{13}C CP/MAS NMR signal intensity from δ 72.5 to 78.5 ppm calculated for (a) cellulosic—periodate oxidized cellulose (LO) and (b) periodate oxidized cellulose (LO)—sulfonated cellulose (LOS)

Samples	ECF HW cellulose	Nanospheres I	Nanospheres II	Whiskers
Cellulose and LO	11.7	8.1	8.7	9.4
LO and LOS	2.2	1.6	1.1	1.6

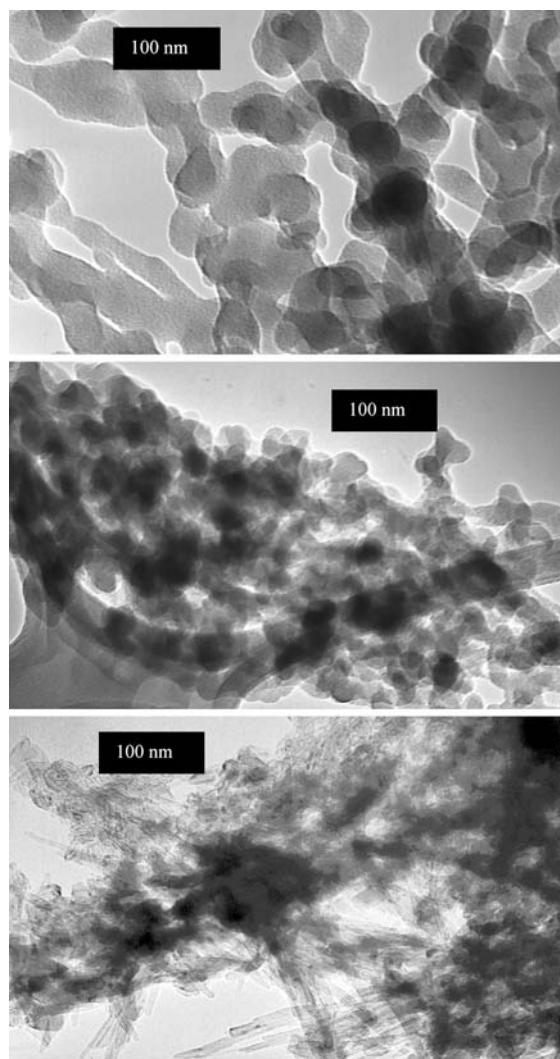
Table 4 Dimensional measurement of ECF hard wood kraft pulp and chemically derived samples

Samples	Arithmetic FQA length (mm)
ECF HW cellulose (C0)	0.81
ECF HW cellulose LO (C0LO)	0.79
ECF HW cellulose HO (C0HO)	0.74
ECF HW cellulose LOS (C0LOS)	0.77
ECF HW cellulose HOS (C0HOS)	0.68

Table 5 Dimensional measurements based on TEM and Zetasizer data and dimensional measurements of whisker based on TEM data and average RMS roughness measurement of cellulosic samples

Samples	Dimension (nm)	Average RMS roughness
ECF HW cellulose (C0)		12.33 ± 3.2
ECF HW cellulose LO (C0LO)		12.29 ± 2.8
ECF HW cellulose LO (C0LOS)		14.12 ± 6.6
Cellulose nanospheres I (C1)	360	3.65 ± 0.2
Cellulose nanospheres I LO (C1LO)	265	6.55 ± 1.5
Cellulose nanospheres I LOS (C1LOS)	180	7.23 ± 2.9
Cellulose nanospheres II (C2)	80	
Cellulose nanospheres II LO (C2LO)	50	
Cellulose nanospheres II LOS (C2LOS)	45	
Cellulose whiskers (C3)	300	3.39 ± 0.5
Cellulose whiskers LO (C3LO)	270	4.17 ± 0.7
Cellulose whiskers LOS (C3LOS)	240	6.88 ± 3.9

of fibrils. The latter samples exhibited slightly elevated RMS roughness value as summarized in Table 5. The amplitude images of the cellulose nanosphere series indicates that the starting nano-cellulose is made up of somewhat elongated particles, while the oxidized samples and sulfonated

**Fig. 1** TEM images of, from top to bottom, cellulose nanospheres II 80 nm (C2), oxidized nanospheres (C2LO), and sulfonated nanospheres (C2LOS)

samples appear to be shorter than the control (Fig. 2). The RMS roughness of the cellulose nanospheres increased with treatment (Table 5). The cellulose whiskers were found to be long, narrow particles with low RMS roughness values.

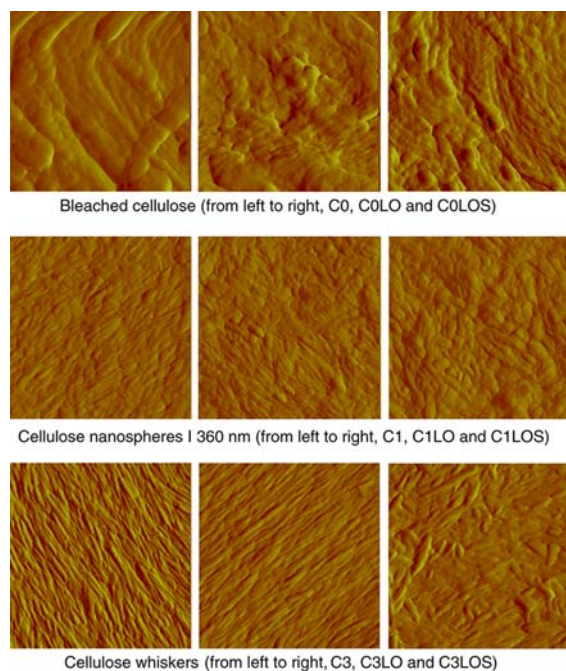


Fig. 2 AFM images of a series of cellulosic materials

The treated whiskers were observed to be about as long as the controls, but wider (Fig. 2). The RMS roughness measurements are higher than the control, but still quite low (Table 5).

As a consequence of oxidation and sulfonation, it can be seen that the surface morphology of the samples was impacted during these modifications.

The water retention values for all of the cellulose samples reported in this study are summarized in Table 2. This data indicates a general decrease in WRV of the oxidized cellulose samples, with the exception for the WRV of cellulose nanospheres I HO (C1HO), which is only slightly higher than that of the nanospheres I (C1). Overall the sulfonated cellulose samples exhibited a considerable increase in water retention values ranging from 8.0% up to nearly a 3-fold increase for both the low and high sulfonated cellulose samples due to the increase of the total acid groups. It can be observed that the nanoscaled samples had higher water retention values than the ECF HW pulps, especially for the low sulfonated cellulose samples. This may be due to their smaller sizes, and thus increased surface area of these nanocellulosic samples, and also because the corresponding sulfonated cellulose samples had higher total acid groups, as shown in Table 2. However, as the total acid group value of the nanosamples

increased, the water retention values decreased and a gel-like material was obtained after sulfonation. Studies by Ulbrich and Parsons of polymeric hydrogels have reported that gel-like properties reduce water retention values (Wack and Ulbricht 2007; Waring and Parsons 2001).

As a result of this study, cellulosic macro fiber and nanoparticles with enhanced water retention properties were obtained by modifying their chemical functionalities. Herein, all the cellulose samples were first oxidized to increase their aldehyde content and then sulfonated to increase the total acid group content of cellulose samples which improved their water absorption properties. As shown in Table 2, by increasing the total acid group content of the cellulose samples using this oxidation/sulfonation protocol improved water retention values could be accomplished. However, the water retention values of the modified cellulose samples began to decrease after certain point, probably due to these chemical procedures, and the changes in morphology associated with the changes in chemistry.

Conclusions

Cellulose samples of various forms were oxidized and sulfonated in this study. The derivatization of cellulose samples increased total acid groups, and also induced dimensional and morphological changes. As a result, some sulfonated cellulose samples were shown to possess higher water retention values, and thus are good candidates as superabsorbent biodegradable cellulose samples. Gel-blocking properties developed for heavily sulfonated cellulose samples and decreased water retention values.

Acknowledgments We are grateful to KCC and NSF (EEC-0332554) for support of these studies. We also want to express our gratitude to K. Nelson and Dr. D.H. Kim from IPST@GA Tech for their valuable suggestions.

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